Bistability in the Oxidation of Arsenite by Iodate in a Stirred Flow Reactor

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Abstract: The reaction between arsenite and iodate at 25 °C and pH 2.25 in a stirred tank reactor exhibits bistability over a range of flow rates and input arsenite and iodate concentrations. Observed steady-state I\(^+\) and I\(^-\) concentrations and points of transition between bistable and unistable behavior are in excellent agreement with values calculated from a simple model

The approach outlined above has at least two virtues. The model is sufficiently simple and general that, unlike more detailed models of chemical oscillation,\(^{11-13}\) it can be applied directly to a wide range of reactions. Secondly, it splits the task of finding new oscillating systems into two more tractable subproblems, the discovery of bistable systems and the design of suitable feedback reactions.

In this paper we report a series of experiments on the behavior of acidic mixtures of arsenite and iodate in a CSTR. The system exhibits bistability over a significant range of input concentrations and flow rates. Similar results have also been obtained by Papsin et al.\(^{14}\) We show here that calculations with a simple model consisting of three overall reaction steps yield results in excellent agreement with our experiments. In further papers we shall present studies of other bistable systems as well as of the detailed coupling of the arsenite–iodate reaction with the chlorite–iodide system to generate oscillation.

Experimental Section

The apparatus consists of a thermally regulated stirred tank glass (Pyrex) flow reactor\(^{13}\) connected to a Sage Model 375A peristaltic pump which allows for one to four independent input flows. The constraints or variables controlled by the experimenter in this system are the temperature, which was maintained at 25.0 ± 0.1 °C in this series of experiments, the residence time \(T\), and the concentrations \([A]_0\) that each input species \(A\) would attain in the tank if no reaction took place. Measurements were made of the potential of an Orion iodide-specific electrode with respect to a mercury–mercurous sulfate reference electrode and of the absorbance at 460 nm, the wavelength of maximum absorbance of I\(^2\). Iodide concentrations are calculated by assuming that I\(^2\) is the only species which absorbs significantly at this wavelength. When nonnegligible concentrations of iodide ion are present, accurate [I\(^-\)] values perturb the stability of the two stable branches on a suitable time scale so as to generate oscillation.

The reaction between arsenite and iodate at 25 °C and pH 2.25 in a stirred tank reactor exhibits bistability over a range of flow rates and input arsenite and iodate concentrations. Observed steady-state I\(^+\) and I\(^-\) concentrations and points of transition between bistable and unistable behavior are in excellent agreement with values calculated from a simple model consisting of three overall component processes: (A) \(I_2^+ + 3H_2AsO_3 = I^- + 3H_2AsO_4^\text{2-}\) (B) \(I_2O_7^\text{2-} + 5I^- + 6H^+ = 3I_2 + 3H_2O\) (C) \(I_2 + H_2AsO_3 + H_2O = 2I^- + H_2AsO_4^\text{2-} + 2H^+\). Implications for the recently discovered arsenite–iodate–chlorite-oscillating reaction are discussed.

Studies of oscillating chemical reactions and related phenomena are of fundamental and rapidly increasing interest both because of the light they shed on the complexities of dynamic behavior possible for systems far from equilibrium and because they may provide experimentally tractable models for some of the endogenous rhythms observed in living systems. The ability of chemists to develop and test general theories of chemical oscillation has been hindered somewhat by the paucity of examples. In spite

We then make use of a simple dynamical model developed by Boissonade and De Kepper,\(^{10}\) which suggests that oscillations can result from the application of an appropriate feedback step to an intrinsically bistable system. The next step in the search for oscillation is to seek a reaction which perturbs the stability of the two stable branches on a suitable time scale so as to generate oscillation.
we show that analysis of the reaction in terms of the component investigation of the total reaction appears to have been carried out and Cullis.21 studies, notably those of Pendlebury and Smith,24 augmented and he proposed an alternative scheme. Further experimental construct a chronometric technique for the determination of small for the variety of complex rate laws observed for this reaction have multistep reaction equals the equilibrium quotient expression since the work of Eggert and ScharnowI6 in 1921. In this paper studies since the early years of this century. Reaction components processes A and B, iodate leaves the reactor not only in the output flow but also by evaporation from the solution. This effect, which depends upon such factors as the stirring and aspiration rates, is by no means insignificant and can be experimentally characterized by monitoring the exponential decay of optical density for an iodine solution in the CSTR at zero flow. We take k_0 to be the associated first-order rate constant. The rate equations for the four independent species in our model are thus

\[ d[IO_3^-]/dt = -r_A - r_B + k_0[IO_3^-]_o - k_0[IO_3^-] \]  
\[ d[1^+]/dt = r_A - 5r_B + 2r_C + k_R[IO_3^-]_o - k_0[1^+] \]  
\[ d[I^-]/dt = 3r_B - 2r_C - k_0[I^-]_o - k_0[I^-] \]  
\[ d[H_2AsO_4^-]/dt = -3r_A - r_C + k_0[H_2AsO_4^-]_o - k_0[H_2AsO_4^-] \]  

where the rates \( r_A, r_B, \) and \( r_C \) are given by eq 2-4. Note that inclusion of the evaporation term \( -k_0[I^-]_o \) in eq 7 makes \( [I^-]_o \) an independent variable. In the absence of such a term, one could calculate \( [I^-] \) from a knowledge of \([IO_3^-] \) and \([1^+] \). The model contains six "free" parameters, \( k_A, k_B, k_D, k_C, k_0, \) and \( [H_2AsO_4^-]_o \) as well as the constraints \( k_0[IO_3^-]_o, [H_2AsO_4^-]_o \), and \([H_2AsO_4^-] \). The experiments were simulated numerically by integrating eq 5-8 with the use of the GEAR algorithm25 for coupled sets of stiff

\[ \text{Model and Method of Calculation} \]

The model we employ for simulating our experiments consists of three irreversible overall processes, A, B, and C.25 The [H^+] concentration is assumed to be constant at \( 6 \times 10^{-3} \) M. Triodide formation is not taken into consideration; the only iodine-containing species in the model are \( IO_3^- \), \( 1^+ \), and \( I^- \).

For process A, we take the rate law, in agreement with Eggert and Scharnow,16 to be

\[ r_A = k_A[IO_3^-][H_2AsO_4^-] \]  

Eggert and Scharnow's assumed rate law for process B consists of a single term proportional to \( [1^+] \) and \([IO_3^-] \), with an unspecified \([H^+] \) dependence. Later studies of the Dushman reaction, recently summarized by Liebhafsky and Roe,20 have yielded a variety of rate laws, most of them involving terms of the form

\[ r_B = k_B[H^+]^a[IO_3^-][1^+][IO_3^-][1^+] \]  

Our calculations show that inclusion of the second term on the right-hand side of eq 3 is essential for bistability.

No discussion of the rate of process C is given by Eggert and Scharnow, other than to note that it must be rapid. We employ the rate law given by Roebeck,22 assuming rapid equilibrium among \( I_3^-, I_2^-, \) and \( I^- \), so that triodide may be eliminated from the expression.

\[ r_C = k_C[H_2AsO_4^-][I_2^-] \]  

In addition to the chemical processes A, B, and C, several physical processes must also be taken into consideration. Iodate, arsenite, and iodide flow into the reactor at rates \( k_0[IO_3^-]_o, k_R[H_2AsO_4^-]_o, \) and \( k_0[IO_3^-]_o \) respectively, where \( k_0 \) is the reciprocal of the residence time \( \tau \) and \( \alpha \) is the fraction of iodide impurity in the iodate.26 Each nonvolatile species X flows out of the reactor at rate \( k_0[X] \), while iodine leaves the reactor not only in the output flow but also by evaporation from the solution. This effect, which depends upon such factors as the stirring and aspiration rates, is by no means insignificant and can be experimentally characterized by monitoring the exponential decay of optical density for an iodine solution in the CSTR at zero flow. We take \( k_0 \) to be the associated first-order rate constant. The rate equations for the four independent species in our model are thus

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differential equations. Typically, starting values for \([\text{IO}_3^-], \text{I}^-, \text{I}_2, \text{and} \ [\text{H}_3\text{AsO}_3]\) were taken as \([\text{IO}_3^-]_0, \alpha [\text{IO}_3^-]_0, 0, \text{and} \ [\text{H}_3\text{AsO}_3]_0\), respectively, for the first flow rate at a given set of input flow concentrations, and the initial concentrations for each subsequent flow rate were the final steady-state concentrations obtained from eq 5-8 when the flow rate with \([\text{I}^-]_0 < \text{I}_0\).

Arrows indicate transitions from one steady state to the other as the flow rate is varied. (At all values of the constraints, different sets of steady-state concentrations may be found depending upon the initial conditions. Such multistability implies that the algebraic equations for the steady state have two or more different stable solutions.)

**Results**

**Bistability.** In the CSTR, the arsenite–iodate system may exhibit either of two stable steady states. The first of the states, which we designate SSI, is the continuation of the thermodynamic branch or equilibrium state which appears at zero flow rate. It is distinguished by relatively high values of \([\text{I}^-]_{SS}\) as measured by the iodide-selective electrode and high \([\text{I}_2]_{SS}\) as given by the absorbance at 460 nm. The other state, SSII, is the extension of the flow branch; i.e., the state which appears in the limit that the flow rate vastly exceeds the chemical reaction rates, so that the steady-state concentrations essentially follow those of the input flows. This state shows relatively low values of both \([\text{I}^-]_{SS}\) and \([\text{I}_2]_{SS}\).

For certain values of \([\text{IO}_3^-]_0, [\text{H}_3\text{AsO}_3]_0, \text{and} \ k_0\) either state SSI or SSII may exist. Which one is actually observed depends upon the initial conditions of the system. Transitions from one state to the other may be induced by a suitable transient perturbation, e.g., injection into the CSTR of a small amount of some species or a temporary change in the flow rate. The system is thus bistable.

In Figure 1, we show the \([\text{I}^-]_{SS}\) and \([\text{I}_2]_{SS}\) values as functions of \(k_0\) for the two steady states under conditions for which the region of bistability covers nearly the entire range of flow rates (0 ≤ \(k_0\) ≤ 1.1 × 10^{-2} s^{-1}) accessible with our pump. If one starts from the maximum flow rate, the system settles into SSII and remains in that state, with \([\text{I}^-]_{SS}\) increasing continuously as the flow rate is lowered, until \(k_0\) reaches 2.2 × 10^{-4} s^{-1} (\(\tau = 4440\) s). If the flow rate is lowered further, both \([\text{I}^-]_{SS}\) and \([\text{I}_2]_{SS}\) undergo discontinuous jumps to the SSI values shown. If the flow rate is then increased, \([\text{I}^-]_{SS}\) and \([\text{I}_2]_{SS}\) vary smoothly until \(k_0\) is changed from 9.0 × 10^{-3} s^{-1} to 11 × 10^{-3} s^{-1}, at which point a transition from SSI back to SSII is observed.

**Figure 1.** Experimentally determined \([\text{I}_2]_{SS}\) and \([\text{I}^-]_{SS}\) as a function of flow rate with \([\text{IO}_3^-]_0 = 1.33 \times 10^{-2} \text{ M and} \ [\text{H}_3\text{AsO}_3]_0 = 2 \times 10^{-3} \text{ M. Arrows indicate transitions from one steady state to the other as the flow rate is varied. (At all values of the constraints, different sets of steady-state concentrations may be found depending upon the initial conditions. Such multistability implies that the algebraic equations for the steady state have two or more different stable solutions.)**

**Figure 2.** Transition by perturbation between steady states with \([\text{IO}_3^-]_0 = 1.33 \times 10^{-3} \text{ M,} \ [\text{H}_3\text{AsO}_3]_0 = 2 \times 10^{-3} \text{ M, and} \ k_0 = 1/\tau = 2.2 \times 10^{-4} \text{ s}^{-1}. \text{At points A and B SSII is perturbed by sudden injections of KI into the CSTR to produce initial increases in} [\text{I}^-] \text{of} 1.3 \times 10^{-4} \text{ and} 3 \times 10^{-4} \text{ M, respectively. At points C and D SSI is perturbed by rapid additions of NaOH inducing sudden increases in} [\text{OH}^-] \text{of} 3 \times 10^{-4} \text{ and} 12 \times 10^{-4} \text{ M, respectively.**

\[(29)\text{Concentrations with subscripts SSI refer to steady-state concentrations. Where ambiguity may arise, subscripts SSI or SSII will be used. (30) \text{We take} \epsilon_\text{I} \text{at} 460 \text{ nm as} 770 \text{ cm}^{-1} \text{ M}^{-1}. (31)\]
second part of the figure, by addition of NaOH.

More complete summaries of the stability of and concentrations in the two states as functions of $k_0$ are shown in Figures 3 and 4, which illustrate the behavior of the system as the constraints $[\text{H}_3\text{AsO}_3]$ and $[\text{IO}_3^-]$ values, respectively, are varied. As Figure 3 shows, at $[\text{IO}_3^-] = 2 \times 10^{-3}$ M, SSII is stable over a wide range of $k_0$ (though, as in Figure 1, it must yield to the thermodynamic branch SSII at sufficiently low flow rates). Decreasing the input flow of arsenite narrows the region of stability of SSII presumably because the $I^-$ and $I_2$ producing processes proceed more slowly and are thus overtaken by the flow at relatively lower values of $k_0$. This interpretation is further supported by Figure 4, which shows that SSII also has a narrower region of stability when $[\text{IO}_3^-]$ is low. At very high iodate inputs, SSII becomes stable only at relatively high flow rates, because processes A and B produce $I^-$ and $I_2$ at a rapid rate, and these species must be depleted by the output flow in order for SSII to be stable.

Finally, the experimental and calculated stabilities of the steady states are summarized in the phase diagrams of Figures 5 and 6, which show the $([\text{H}_3\text{AsO}_3], k_0)$ and $([\text{IO}_3^-], k_0)$ constraint planes, respectively. One must bear in mind that for all input concentrations, only SSII can be stable in the limit $k_0 \rightarrow 0$, and only SSII stability can be observed as $k_0 \rightarrow \infty$.

Stoichiometry. Our analysis of the reaction in terms of the three component processes A, B, and C implied that when $[\text{H}_3\text{AsO}_3]/[\text{IO}_3^-] < 3$, the net reaction is given by eq 1, with 2 mol of iodate consumed for every 5 mol of arsenite and $I_2$ as the major product. When arsenite is in excess, process C consumes the remaining $I_2$, and the product is $I_1$, with the stoichiometry being that of process A.

Figures 7 and 8 show $[I^-]_{\text{SSI}}$ and $[I_2]_{\text{SSI}}$ as functions of the input concentrations, support this view. In Figure 7, $[I_2]_{\text{SSI}}$ is seen to increase to a maximum with increasing $[\text{H}_3\text{AsO}_3]$ until the stoichiometric ratio of eq 1, $[\text{H}_3\text{AsO}_3]/[\text{IO}_3^-] = 2.5$, is reached. The steady-state iodide concentration then decreases sharply until, when the limiting arsenite–iodate ratio of 3:1 is reached, $[I_1]_{\text{SSI}}$ becomes essentially zero as the stoichiometry becomes that of process A. The figure also shows that $[I^-]_{\text{SSI}}$ rises with increasing arsenite until at the 3:1 ratio a limiting value of $[I^-]_{\text{SSI}} = [\text{IO}_3^-]_0$ is approached. In Figure 8, we see that as iodate is increased at fixed arsenite, $[I_2]_{\text{SSI}}$ approaches a limiting value qualitatively consistent with that given by eq 1 in the case of excess iodate, while $[I^-]$ decreases almost linearly on this log–log plot.

Dynamics. The major part of our investigation has concentrated on the nature and stability of the steady states. This focus has the advantage of yielding reproducible results which are sufficiently

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**Figure 3.** Experimentally determined absorbance in SSII and $[I^-]_{\text{SSI}}$ as functions of flow rate with $[\text{IO}_3^-]_0 = 2 \times 10^{-3}$ M for $([\text{H}_3\text{AsO}_3])$ values given by symbols: $\circ = 12 \times 10^{-3}$ M, $\triangle = 6.0 \times 10^{-3}$ M, $\Delta = 5.5 \times 10^{-3}$ M, $\triangledown = 5.0 \times 10^{-3}$ M, $\times = 4.0 \times 10^{-3}$ M, $\bullet = 2.0 \times 10^{-3}$ M. Sunburst for $[H_3AsO_3]$ values given by symbols: $\square = 0.5 \times 10^{-3}$ M, $\circ = 0.5 \times 10^{-3}$ M. Absorbance in SSII is too small to measure.

**Figure 4.** As in Figure 3, but with $([\text{H}_3\text{AsO}_3]) = 2 \times 10^{-3}$ M for $[\text{IO}_3^-]_0$ values given by symbols: $\square = 85.3 \times 10^{-3}$ M, $\bullet = 21.3 \times 10^{-3}$ M, $\times = 5.3 \times 10^{-3}$ M, $\triangledown = 2.0 \times 10^{-3}$ M, $\Delta = 1.0 \times 10^{-3}$ M, $\triangle = 0.67 \times 10^{-3}$ M, $\circ = 0.33 \times 10^{-3}$ M.

**Figure 5.** A portion of the phase diagram in the $([\text{H}_3\text{AsO}_3], k_0)$ constraint plane. Symbols: $\Delta$, SSII stable; $\triangledown$, SSII stable; $\times$, bistability SSII/SSI. Solid lines indicate boundaries of the bistable region calculated using the model. All other constraints are kept constant with $[\text{NaIO}_3]_0 = 2 \times 10^{-3}$ M.
sensitive and extensive to make possible the testing of proposed models. Nevertheless, both the experiments and our calculations generate a great deal more data in the form of I- concentrations and absorbance or I2 concentrations as functions of time.

One interesting dynamic phenomenon which appears in our system and in other reactions in flow systems is the emergence of overshoots and undershoots when the external constraints on the system are changed. In Figure 9, we show the experimental and calculated response of [I2] to sudden variations in the flow rate. Note the excellent qualitative agreement. Overshoots and undershoots are also observed when stepwise changes are made in [H3AsO3] at a fixed flow rate. No overshoots and undershoots are observed, however, when [IO3]- is varied in an analogous manner.

It has also been suggested that dynamic data analyzed in terms of the spectrum of relaxation times, when a system in a CSTR returns to a steady state after perturbation, can yield useful chemical information. We agree that the dynamic behavior of CSTR systems does indeed contain much information of significance, though more thorough theoretical analyses will probably be required to extract it.

Discussion

The model we have employed for the arsenite–iodate reaction is a crude one in that no attempt is made to dissect the component processes into elementary steps. Nevertheless, the model gives regions of stability of the steady states in almost perfect agreement with experiment and predicts the trends in both sets of steady-state concentrations correctly as well as yielding qualitative values of concentrations in the more easily measurable SSI to surprising accuracy. The model also has the virtues of providing some qualitative understanding of the origin of the bistability and of being sufficiently simple that one can extract the effects of the various free parameters on the system behavior.

We have outlined above the view that bistability results from a balance between the rate of chemical reaction, which tends to stabilize SSI, and the rate of flow in and out of the reactor, which

favors SSII. Factors which increase the reaction rate will generally tend to extend the region of stability of SSII to higher flow rates and/or to shift to higher flow rates the lower limit of SSII stability.

In Table I we give the final values arrived at for our six “free” parameters. These values were established by our own direct experimental measurement where possible, augmented by the use of rate constants available in the literature and finally, where necessary, adjustment of parameters to give the best agreement between our calculated and experimental results.

Figures 3 and 4 show, [I\textsubscript{2}]\textsubscript{SSII} exhibits a maximum as a function of k\textsubscript{B2} for nearly all sets of input concentrations. In an initial set of calculations carried out before we became aware of the effects of iodine evaporation (k\textsubscript{B1} = 0), [I\textsubscript{2}]\textsubscript{SSII} was generally about 3 times higher than the results obtained by allowing for evaporation and decreased monotonically with k\textsubscript{B1}.

Table I. Values of the “Free” Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Method of determination</th>
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<tbody>
<tr>
<td>k\textsubscript{A}</td>
<td>1 \times 10^{-11} M\textsuperscript{-1} s\textsuperscript{-1}</td>
<td>Experimental upper limit from initial rate of I\textsuperscript{-} formation, calculated effect on SSII stability</td>
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<tr>
<td>k\textsubscript{B1}</td>
<td>8 \times 10\textsuperscript{3} M\textsuperscript{-3} s\textsuperscript{-1}</td>
<td>Reference 20, necessary for bistability, calculated effect on SSII stability</td>
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<tr>
<td>k\textsubscript{B2}</td>
<td>5 \times 10\textsuperscript{4} M\textsuperscript{-4} s\textsuperscript{-1}</td>
<td>Reference 24, experimental determined from decay rate of I\textsubscript{2} solution optical density</td>
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<tr>
<td>k\textsubscript{C}</td>
<td>3.2 \times 10\textsuperscript{-3} M\textsuperscript{-1} s\textsuperscript{-1}</td>
<td>Experimental determined from SSII stability</td>
</tr>
<tr>
<td>k\textsubscript{D}</td>
<td>3.4 \times 10\textsuperscript{-1} M\textsuperscript{-1} s\textsuperscript{-1}</td>
<td>Calculated effect on SSII stability</td>
</tr>
<tr>
<td>k\textsubscript{E}</td>
<td>5 \times 10\textsuperscript{-4} M\textsuperscript{-1} s\textsuperscript{-1}</td>
<td>Experimental upper limit from effects of initially added I\textsuperscript{-}, calculated effect on SSII stability</td>
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The value obtained from k\textsubscript{B1} lies between that obtained with classical kinetic techniques by Abel and co-workers\textsuperscript{33-34} and that found by Beran and Bruckenstein\textsuperscript{35} with electrochemical methods employing rotating disk cathodes. Our k\textsubscript{B2} value is intermediate between those determined by electrochemical\textsuperscript{36} and spectrophotometric\textsuperscript{37} techniques. The value of k\textsubscript{B2} strongly influences both the flow rate at which SSII becomes unstable, i.e., the upper limit of bistability, and the values of [I\textsubscript{2}]\textsubscript{SSII}. Thus k\textsubscript{B2} plays a somewhat complementary role to that of k\textsubscript{B1}.

The rate constant for the Roebuck reaction k\textsubscript{C} has much the same effect as k\textsubscript{B2}. That is, increasing k\textsubscript{C} moves the SSII → SSII transition to higher flow rates and increases [I\textsuperscript{-}]\textsubscript{SSII}. We chose for our initial k\textsubscript{C} the rate constant for the term in Pendlebury and Smith’s experimental rate law corresponding to eq. 4. Since this value gave results in excellent agreement with our experiments, no further modification of k\textsubscript{C} was undertaken. Given the simplicity of our model, no attempt was made to include the detailed hydroxyl ion or ionic strength dependence found by Pendlebury and Smith in their stopped flow experiments.

Two reasons can be cited for the sharp disagreement between the k\textsubscript{A} reported by Eggert and Scharnow and the value found here. First, Eggert and Scharnow consider process A as the only source of iodide in the reaction. If their iodate contained any I\textsuperscript{-} impurity, then their reaction time, which they take as the time to the appearance of I\textsubscript{2}, would be decreased, thereby raising their calculated k\textsubscript{A}. Secondly, Eggert and Scharnow employ a single term rate law for the Dushman reaction, ignoring the term second order in [I\textsuperscript{-}], which is dominant when iodide levels exceed 10\textsuperscript{-4}–10\textsuperscript{-3} M. If the rate of process B is underestimated in this manner, then k\textsubscript{A} must be overestimated in order to give the correct reaction time.

Liebhabsky and Roe\textsuperscript{36} summarize a variety of rate studies on the Dushman reaction, process B. They quote values for k\textsubscript{B1} ranging from 4 \times 10\textsuperscript{3} M\textsuperscript{-3} s\textsuperscript{-1} to 3 \times 10\textsuperscript{4} M\textsuperscript{-3} s\textsuperscript{-1} and for k\textsubscript{B2} from 3 \times 10\textsuperscript{4} M\textsuperscript{-4} s\textsuperscript{-1} to 2 \times 10\textsuperscript{4} M\textsuperscript{-4} s\textsuperscript{-1}. Eggert and Scharnow’s value for k\textsubscript{B1} with k\textsubscript{B2} = 0 is 1.6 \times 10\textsuperscript{3} M\textsuperscript{-3} s\textsuperscript{-1}. Our calculations failed to produce bistability with any k\textsubscript{B1}; in this range of the absence of the k\textsubscript{B1} term. This failure is not surprising when one observes that in SSII, [I\textsuperscript{-}] is sufficiently high that the k\textsubscript{B1} term should be small compared with the term second rate order in iodide. The

\[
\alpha = \frac{\Delta \rho}{\Delta \rho_{\text{opt}}}[I\textsubscript{2}]_{\text{opt}}[H\textsubscript{3}AsO\textsubscript{3}]_{0}\cdot \left[H\textsubscript{2}AsO\textsubscript{4}\right]_{0}
\]

The value obtained from eq 9 is 2 \times 10\textsuperscript{-6} M\textsuperscript{-1} s\textsuperscript{-1}, significantly lower than that found by Eggert and Scharnow. Further calculations showed that obtaining the correct region of bistability requires k\textsubscript{A} \leq 1 \times 10\textsuperscript{-11} M\textsuperscript{-3} s\textsuperscript{-1}. Since our calculated values of [I\textsuperscript{-}]\textsubscript{SSII} are lower than our experimental values, k\textsubscript{A} was chosen as this upper limit. However, it is likely that process A could be eliminated entirely from our model and increases in [I\textsuperscript{-}]\textsuperscript{SSII} obtained by appropriate modification of the other parameters.

at all input concentrations. As Figure 10 illustrates, introduction of this evaporation effect into our model indeed yields the observed maximum in $[I_2]_{SS}$. Our calculations give a small but systematic underestimate of the experimentally determined $[I_2]_{SS}$. One reason for this discrepancy may lie in our neglect of triiodide formation. Particularly in $SS$, where $I^-$ is relatively high, some of the iodine in our model will actually be present as nonvolatile $I_2^-$. Equation 7 will then yield an overestimate of the rate of loss of $I_2$ from the system.

The model employed in our calculations ignores many complexities of the full system. The reverse steps of the component processes are omitted; no note is taken of the complex kinetics of the Roebuck reaction; the formation of triiodide and the reactivity of that species are not considered. In spite of these simplifications, remarkably good agreement between our calculations and the experimentally determined steady-state concentrations, phase diagram, stoichiometry, and dynamics have been achieved. It thus appears that the qualitative picture of the reaction suggested by Eggert and Scharnov is correct, despite major quantitative differences between their analysis and ours.

We have not attempted to develop a mechanism for the arsenite–iodate system consisting of a complete set of elementary steps. Any such mechanism must pass the stringent tests of consistency not only with the experimental results presented here but also with the considerable body of data available from batch experiments on the Dushman and Roebuck reactions as well as on the arsenite–iodate reaction itself. Efforts are now under way to construct such a mechanism.

A number of the "free" parameters in our model were either determined experimentally or were taken from other experimental studies in the literature. The remaining constants could be fixed rather accurately by fitting the observed transition points between the two steady states. We suggest that this procedure of choosing rate constants to reproduce experimentally determined phase diagrams in bistable flow systems may prove a useful addition to the kineticist's array of techniques, particularly when the number of unknown parameters is relatively small.

In addition to forming part of the recently discovered arsenite–iodate–chlorite oscillator, the reaction studied here has been shown to propagate waves of chemical reactivity in an initially homogeneous unstirred solution. To date, only three other isothermal, nonbiological homogeneous bistable systems, the Briggs–Rauscher reaction, the cerium–bromate system, and the reaction of bis(trichloromethyl) trisulfide with aniline in methanol, have been treated in the literature. In further papers in this series we shall examine several other cases of bistability in the CSTR, including the chlorite–iodide and the ferrous–nitrate systems. With this considerably expanded range of experimental examples, it may then prove feasible to elucidate some of the actual relations among the phenomena of autocatalysis, bistability, temporal oscillation, and the propagation of spatial waves.

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Synthesis and Characterization of the Major Component of Alamethicin

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Abstract: Natural alamethicin has been purified on a high-performance liquid chromatography (HPLC) system developed to purify and characterize synthetic peptides corresponding to the proposed structures of alamethicin. Five of the twelve components detectable by UV absorption at 210 nm were isolated in pure form and were characterized for their antibacterial and ionophoric properties. Low-resolution electron-impact mass spectrometry (LREIMS) indicates that the purified major component and a synthetic preparation based on the recently proposed structure are identical in their primary structures. This major component, detectable by UV absorption at 210 nm were isolated in pure form and were characterized for their antibacterial and ionophoric properties.

The recently reported primary structure (Figure 1D) of the major component of alamethicin is based on a combination of techniques emphasizing both electron-impact and field-desorption high-resolution mass spectrometry. Alamethicins fall into a special class of peptide antibiotics along with antiamoebins, emermicins, and suzukacinlin termed as “peptaiophophs” Peptides of this class have been found to have several aminosobutyric acid